



## Assessing soil heavy metal pollution in the water-level-fluctuation zone of the Three Gorges Reservoir, China

Chen Ye<sup>a,b</sup>, Siyue Li<sup>a</sup>, Yulong Zhang<sup>a,b</sup>, Quanfa Zhang<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Aquatic Botany and Watershed Ecology, Wuhan Botanical Garden, Chinese Academy of Sciences, Wuhan 430074, China

<sup>b</sup> Graduate School of the Chinese Academy of Sciences, Beijing 100049, China

### ARTICLE INFO

#### Article history:

Received 15 January 2011

Received in revised form 20 April 2011

Accepted 20 April 2011

Available online 27 April 2011

#### Keywords:

Submergence

Heavy metal

Enrichment factor

Source identification

Source apportionment

### ABSTRACT

The water-level-fluctuation zone (WLFZ) between the elevations of 145–175 m in China's Three Gorges Reservoir has experienced a novel hydrological regime with half a year (May–September) exposed in summer and another half (October–April) submerged in winter. In September 2008 (before submergence) and June 2009 (after submergence), soil samples were collected in 12 sites in the WLFZ and heavy metals (Hg, As, Cr, Cd, Pb, Cu, Zn, Fe, and Mn) were determined. Enrichment factor (EF), factor analysis (FA), and factor analysis–multiple linear regression (FA–MLR) were employed for heavy metal pollution assessment, source identification, and source apportionment, respectively. Results demonstrate spatial variability in heavy metals before and after submergence and elements of As, Cd, Pb, Cu, and Zn are higher in the upper and low reaches. FA and FA–MLR reveal that As and Cd are the primary pollutants before submergence, and over 45% of As originates from domestic sewage and 59% of Cd from industrial wastes. After submergence, the major contaminants are Hg, Cd, and Pb, and traffic exhaust contributes approximately 81% to Hg and industrial effluent accounts about 36% and 73% for Cd and Pb, respectively. Our results suggest that increased shipping and industrial wastes have deposited large amounts of heavy metals which have been accumulated in the WLFZ during submergence period.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

Heavy metals are involved in various industrial processes, agricultural activities, domestic wastes, and vehicles emission, and they are considered as one of the most serious pollutants due to their persistence in the environment, bioaccumulation and high toxicity [1–4]. In a landscape, riparian zone is an effective sink for heavy metals due to its integration and accumulation of pollutants from both the terrestrial and aquatic environments [5]. In the non-flood season, heavy metals in the riparian zone generally come from natural weathering and anthropogenic activities, such as riverine discharge, industrial wastewater, and domestic sewage [6,7]. In flood season, heavy metals in the aquatic environment and the inputs from human activities in the uplands can be deposited into the riparian zone by flooding [8]. Therefore, heavy metals in the riparian zone have been affected by flooding through fluvial transport and frequent material exchanges between the aquatic and terrestrial systems [9,10].

Research on heavy metal pollution in the riparian zone has received increasing attention [11–13], and geochemical approaches (*i.e.*, enrichment factor, EF) and multivariate statistical analysis have been widely used [12,13]. EF which is defined as the observed metal to reference metal ratio in the sample of interest divided by the background metal to reference metal ratio, is an index to assess the status and degree of soil heavy metal pollution in the riverine, estuarine, and coastal environments [14,15]. Nevertheless, multivariate statistic analyses, such as factor analysis (FA) and factor analysis–multiple linear regression (FA–MLR) analysis, have been frequently applied to identify pollution sources and quantify their contributions [16,17]. These techniques could offer valuable tools for developing appropriate strategies for effective management of soil and water conservation [18].

With the completion of the Three Gorges Dam, the Three Gorges Reservoir (TGR) inundates a total of area of 1080 km<sup>2</sup>. The water level of the reservoir fluctuates from 145 m a.s.l. in summer (May–September) 2008 to 172 m in winter (October–April), resulting in formation of the water-level-fluctuation zone (WLFZ) with a total area of 350 km<sup>2</sup> in the reservoir [19]. There are concerns that heavy metal from industrial activities and domestic consumption in the uplands may be carried on to and accumulated in the WLFZ by floods [20]. Previous studies have reported that soils in

\* Corresponding author. Tel.: +86 27 87510702; fax: +86 27 87510251.

E-mail addresses: [qzhang@wbcas.cn](mailto:qzhang@wbcas.cn), [syli2006@163.com](mailto:syli2006@163.com) (Q. Zhang).

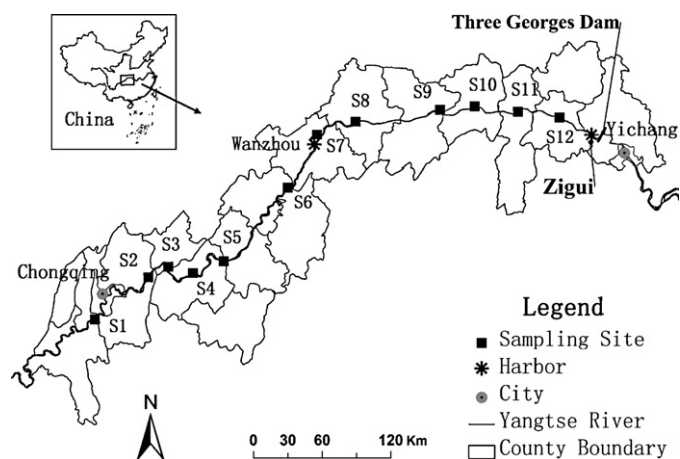


Fig. 1. Location of the sampling sites in the water-level-fluctuation zone of Three Gorges Reservoir, China.

the upstream of the TGR were polluted by industrial wastewater and domestic sewage from Chongqing city with a population of 32 millions and industrial centers in the adjacent area [21–24]. In the downstream of the reservoir, intensive land use has increased non-point pollutants in the reservoir region [24]. However, there is little information available about the heavy metals pollution in the WLFZ and their changes after prolonged submergence.

We hypothesized that the heavy metal concentrations, source profiles, and source distributions had altered after submergence. In this study, EF, FA, and FA-MLR were used in heavy metal pollution assessment, source identification, and source apportionment before and after submergence in the WLFZ. The objective is to help develop soil conservation strategies for the WLFZ and water conservation for the TGR, China.

## 2. Materials and methods

### 2.1. Site description

The TGR region (29°16′–31°25′N, 106°–111°50′E) lies in a 600 km valley from Yichang to upstream Chongqing, a transitional zone from the Tibetan Plateau in the west to the east rolling hills and plains of China's subtropical region (Fig. 1). Its annual mean temperature is 16.5–19 °C, ranging from 3.4–7.2 °C in January to 28–30 °C in July. Annual mean precipitation is about 1100 mm with 80% falling in April–October. Zonal soil is composed of red soil, yellow soil, and mountain yellow soil [25]. With the Three Gorges Dam fully functioning in 2010, the water level in the reservoir fluctuates from 145 m in summer to 175 m in winter. The reversal of flooding time and prolonged submergence duration have dramatically altered the hydrological regime in the WLFZ [26]. Before submergence, vegetation in the WLFZ was dominated by annuals, i.e., *Setaria viridis*, *Digitaria ciliaris*, and *Leptochloa chinensis*, perennials including *Cynodo dactylon*, *Hemarthria altissima*, and *Capillipedium assimile*, and woody plants such as *Ficus tikoua*, *Pterocarya stenoptera*, and *Vitex negundo* [27]. However, after the prolonged submergence, annual plants such as *S. viridis*, *D. ciliaris*, and *L. Chinensis* are dominant species [27], and a few alien invasive plants, such as *Eupatorium adenophorum* and *Alternanthera philoxeroides*, are present in the WLFZ [19].

### 2.2. Soil sampling

Field surveys were conducted in September 2008 and June 2009 when the reservoir's water level was 145 m and the WLFZ

was exposed to the air after submergence. From October 2008 to May 2009, the water level of the reservoir reached 172 m and all the sampling sites were submerged. We selected 12 sampling sites based on the geographical characteristics of the WLFZ from upstream to downstream in the TGR (Fig. 1). In each site, 6 sampling plots (1 m × 1 m each) were randomly selected in the elevation from 145 m to 172 m. However, in site 1, samplings were only collected between the elevations of 165–172 m because of the high water level during the sampling period. At each plot, we collected five top soil samples (i.e., 0–20 cm) and the samples were well mixed to form a composite sample. All the samples were sealed in plastic bags and stored at 4 °C for analysis.

### 2.3. Sample analysis

The concentrations of heavy metals (i.e., Hg, As, Cr, Cd, Pb, Cu, Zn, Fe, and Mn) and total organic carbon (TOC) in soils were analyzed. TOC was determined by titration with FeSO<sub>4</sub> after digestion with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>–H<sub>2</sub>SO<sub>4</sub> solution [13]. For metal analysis, total sediment digestion was performed in Teflon vessels following the classical open digestion procedures with a mixture of concentrated HF–HClO<sub>4</sub>–HNO<sub>3</sub> (i.e., 10 ml HNO<sub>3</sub>, 5 ml HF and 5 ml HClO<sub>4</sub>) [28]. Concentrations of metals in solutions were determined using flame atomic absorption spectrometry (FAAS) (Analytikjena AAS vario6, Germany) for Cr, Cd, Pb, Cu, Zn, Fe, and Mn, and cold vapor AAS for Hg with the method detection limit (MDL) of 0.02 mg kg<sup>-1</sup> [13]. As was determined by diethyl disulfide and carbamate silver colorimetric method (DDC-Ag) with the MDL of 0.05 mg kg<sup>-1</sup>, recommended by the State Environmental Protection Administration of China (GB15618-1995) [29]. Method accuracy and quality control were verified by triplicate analysis of soil reference material (GBW07309). A good agreement was observed between the data analyzed and those certified by the reference material and the analytical precision was within ±10%.

### 2.4. Data analysis

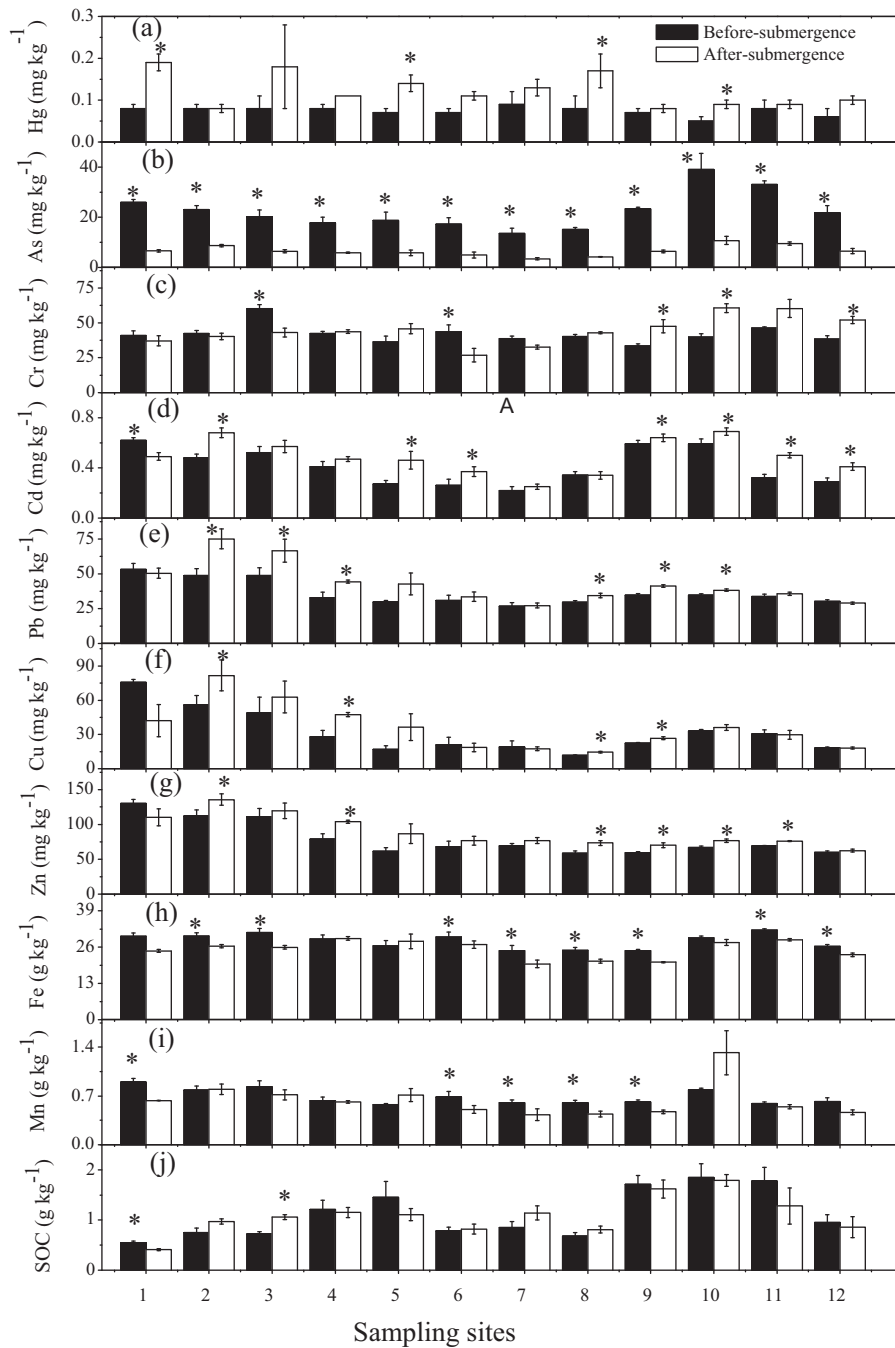
#### 2.4.1. Enrichment factor (EF)

EF is used to evaluate the soil heavy metal pollution status. Because Fe is abundant in soil and is considered to be free from anthropogenic contribution in our study area, it is commonly used for normalization purpose [30]. Fe concentration showing spatial variations is contributable to the spatial differences in geological setting and soils (Fig. 2) [21–24]. Mathematically, EF is expressed as following [30,31]:

$$EF = \frac{(Me/Fe)_{\text{sample}}}{(Me/Fe)_{\text{reference}}} \quad (1)$$

where (Me/Fe)<sub>sample</sub> is the metal to Fe ratio in the sample of interest; (Me/Fe)<sub>reference</sub> is the reference value to Fe ratio. Blaser et al. [32] suggested that local background value as the reference may provide a more meaningful basis for calculating EF than average crust value. Thus, this study used the local background values as reference values, 0.05 mg kg<sup>-1</sup> for Hg, 5.84 mg kg<sup>-1</sup> for As, 78.03 mg kg<sup>-1</sup> for Cr, 0.13 mg kg<sup>-1</sup> for Cd, 23.88 mg kg<sup>-1</sup> for Pb, 25.00 mg kg<sup>-1</sup> for Cu, and 69.88 mg kg<sup>-1</sup> for Zn [33]. The reference values of Fe and Mn were 29,400 mg kg<sup>-1</sup> and 583 mg kg<sup>-1</sup>, respectively [34].

The EF value has been used to evaluate anthropogenic influences on heavy metal pollution [13]. Zhang and Liu [35] recommended using EF=1.5 as an assessment criterion. When EF values are between 0.5 and 1.5, it suggests that the trace metals might be entirely from crustal materials or natural weathering, while an EF value greater than 1.5 suggests that a significant portion



**Fig. 2.** Spatial variations in heavy metals and soil organic carbon (SOC) in the 12 sampling sites (mean  $\pm$  SE). Note: \* indicating statistically significant differences between the two sampling times (before submergence and after submergence) at  $p = 0.05$  level.

of the trace metal is delivered from non-crustal materials [35]. Additionally, Han et al. [36] suggested that a trace metal element with an EF value less than 2 was not a major concern pollutant.

#### 2.4.2. Statistical analysis

Paired-samples *T* test was performed to compare the trace metal concentrations before and after submergence. Two-way ANOVA was used to examine the spatial and temporal variations of the elements. Multivariate analyses including factor analysis (FA) and multiple linear regression on factor analysis (FA-MLR) were used to identify their sources and quantify their contributions, respec-

tively [37]. FA provided qualitative information about the sources of the contaminant. The multiple regression method was used following the FA, which was named as FA-MLR for supplying quantitative information about the contributions of each source type. The accuracy of the FA-MLR was tested by calculating "estimated to observed" ratios of the elements [37,38]. Prior to the multivariate analysis, data were standardized by ln-transformation to minimize the effects of differences in measurement units [38]. Kaiser–Meyer–Olkin (KMO) and Bartlett's sphericity test were conducted to examine the suitability of the data for factor analysis [39]. All the processes were performed using SPSS 13.0 for windows.

**Table 1**  
Statistically significant differences of heavy metals based on two-way ANOVA.

Variables	Hg	As	Cr	Cd	Pb	Cu	Zn	Fe	Mn	SOC
Sampling sites	n.s.	***	***	***	***	***	***	***	***	***
Time	***	***	n.s.	***	***	*	***	***	n.s.	n.s.
Sampling sites × Time	n.s.	***	***	**	**	*	n.s.	n.s.	**	n.s.

Note: n.s.: not significant; Time: before and after submergence.

\*  $p < 0.05$ .

\*\*  $p < 0.01$ .

\*\*\*  $p < 0.001$ .

### 3. Results

#### 3.1. Spatial pattern of heavy metals

All the heavy metals excepting Hg show significantly spatial variation in the 12 sampling sites ( $p < 0.001$ ) (Table 1), and the concentrations of As, Cd, Pb, Cu, and Zn are higher in the upper (sites 1–4) and low reaches (sites 9–12) than those in the middle reach (sites 5–8), both before and after submergence (Fig. 2). Enrichment factor analysis also indicates spatial variability with higher values in the upper and low reaches, *i.e.*, As and Cd with EF values greater than 2 in the upper and low reaches, and EF (Pb), EF (Cu), EF (Zn), and EF (Mn) greater than 1.5 in the upper reach before and after submergence (Table 2).

#### 3.2. Changes in heavy metals after submergence

The concentrations of Hg, Cd, Pb, Cu, and Zn significantly increase, and As and Fe decrease after submergence ( $p < 0.001$ ) (Tables 1 and 3). The average EF (Hg) is  $1.73 \pm 0.11$  before submergence and changes to  $3.20 \pm 0.35$  after submergence, and EF (As) decreases from  $3.98 \pm 0.34$  before submergence to  $1.30 \pm 0.10$

after submergence (Table 2). The mean EF values of heavy metals decrease in the order of  $As > Cd > Hg > Pb > Cu > Mn > Zn > Cr$  before submergence, and the order is  $Cd > Hg > Pb > Cu > Zn > As > Mn > Cr$  after submergence (Table 2).

### 4. Discussion

#### 4.1. Spatial variations of heavy metals

The significantly spatial variability of heavy metals in the WLFZ ( $p < 0.001$ ) (Table 1 and Fig. 2) before and after submergence indicates great impacts on heavy metals by anthropogenic activities, *i.e.*, point sources such as chemical industry and domestic sewage runoff [18]. As, Cd, Pb, Cu, and Zn in the upper reach (sites 1–4) might be correlated to the industrial activities and municipal sewage discharges from Chongqing city, with developed economy and high dense population (Fig. 1) [13]. Heavy metals in the low reach (sites 9–12) (Fig. 2) are attributable to agriculture in this region, which is consistent with previous study [28]. Moreover, a few heavy metals (*i.e.*, Cr, Cu, and Zn) with higher concentrations in the low reach could also be contributable to the natural weathering

**Table 2**  
Enrichment factor (EF) of heavy metals in the water-level-fluctuation zone of the Three Gorges Reservoir, China.

	EF(Hg)	EF(As)	EF(Cr)	EF(Cd)	EF(Pb)	EF(Cu)	EF(Zn)	EF(Mn)
(a) Before submergence								
Site 1	1.82	4.36	0.52	4.55	2.19	2.99	1.84	1.52
Site 2	1.70	3.86	0.53	3.51	1.99	2.19	1.57	1.31
Site 3	1.68	3.28	0.73	3.69	1.92	1.82	1.51	1.33
Site 4	1.85	3.02	0.56	3.05	1.38	1.12	1.14	1.10
Site 5	1.84	3.46	0.51	2.22	1.41	0.74	0.99	1.13
Site 6	1.53	2.91	0.55	1.87	1.28	0.82	0.96	1.15
Site 7	2.63	2.89	0.61	1.86	1.35	0.90	1.21	1.25
Site 8	1.98	3.08	0.62	3.02	1.47	0.56	1.00	1.23
Site 9	1.74	4.76	0.51	5.31	1.73	1.06	1.01	1.26
Site 10	1.00	6.75	0.51	4.44	1.46	1.32	0.96	1.36
Site 11	1.59	5.22	0.55	2.23	1.30	1.11	0.91	0.93
Site 12	1.45	4.20	0.55	2.42	1.42	0.82	0.96	1.19
Minimum	1.00	2.89	0.51	1.86	1.28	0.56	0.91	0.93
Maximum	2.63	6.75	0.73	5.31	2.19	2.99	1.84	1.52
Mean	1.73	3.98	0.56	3.18	1.58	1.29	1.17	1.23
SE	0.11	0.34	0.02	0.33	0.09	0.20	0.09	0.04
(b) After submergence								
Site 1	4.86	1.34	0.57	4.41	2.53	2.04	1.89	1.30
Site 2	1.99	1.65	0.58	5.63	3.48	3.62	2.16	1.52
Site 3	4.35	1.26	0.63	4.83	3.16	2.85	1.94	1.39
Site 4	2.35	1.00	0.57	3.57	1.88	1.92	1.51	1.07
Site 5	3.21	1.00	0.63	3.50	1.82	1.39	1.26	1.31
Site 6	2.66	0.89	0.36	2.98	1.52	0.80	1.19	0.94
Site 7	4.30	0.90	0.63	2.80	1.71	1.07	1.64	1.05
Site 8	5.46	1.02	0.77	3.48	2.01	0.81	1.47	1.06
Site 9	2.49	1.56	0.87	6.85	2.46	1.52	1.43	1.15
Site 10	2.04	1.93	0.82	5.51	1.71	1.53	1.17	2.35
Site 11	2.05	1.68	0.80	3.83	1.53	1.22	1.12	0.96
Site 12	2.63	1.40	0.84	3.89	1.54	0.91	1.13	1.01
Minimum	1.99	0.89	0.36	2.80	1.52	0.80	1.12	0.94
Maximum	5.46	1.93	0.87	6.85	3.48	3.62	2.16	2.35
Mean	3.20	1.30	0.67	4.27	2.11	1.64	1.49	1.26
SE	0.35	0.10	0.04	0.35	0.19	0.25	0.10	0.11

**Table 3**  
Heavy metal concentrations (mg kg<sup>-1</sup>; mean ± SE) in the Three Gorges Reservoir region, China.

Region	Hg	As	Cr	Cd	Pb	Cu	Zn	Reference
Cultivated soil in the riparian zone	0.07 ± 0.01	7.48 ± 0.74	49.41 ± 1.64	0.39 ± 0.07	48.18 ± 2.83	21.14 ± 1.89	84.75 ± 2.95	[2]
Water-level-fluctuation zone	0.06 ± 0.04	8.65 ± 2.23		0.32 ± 0.27	29.3 ± 13.20	37.00 ± 22.20	72.70 ± 12.70	[22]
Draw-done zone	0.04 ± 0.05	5.50 ± 2.36		0.29 ± 0.17	21.66 ± 8.42	29.42 ± 18.31	82.46 ± 24.87	[23]
Agriculture soil					25.45 ± 8.80	29.96 ± 12.80	64.79 ± 18.79	[45]
Reservoir region	0.06 ± 0.18	7.40 ± 4.54	79.40 ± 23.40	0.21 ± 0.16	25.30 ± 4.54	23.50 ± 8.09	71.60 ± 14.90	[24]
Background values	0.05	5.84	78.03	0.13	23.88	25.00	69.88	[33]
Water-level-fluctuation zone in 2008 (before submergence)	0.07 ± 0.00	22.24 ± 1.16	41.99 ± 1.06	0.40 ± 0.02	35.41 ± 1.26	29.78 ± 2.52	76.57 ± 3.05	This study
Water-level-fluctuation zone in 2009 (after submergence)	0.12 ± 0.01	6.59 ± 0.34	44.72 ± 1.51	0.49 ± 0.02	42.89 ± 2.06	35.70 ± 3.10	88.09 ± 3.21	This study

because the EF values lower than 1.5 (Table 2), and these elements have high background values in the region [33,35].

#### 4.2. Pollution assessment

EF has been widely used to evaluate anthropogenic influences to heavy metals pollution in soils and sediments [13]. In this study, the average EF of Hg, Pb, Cu, Zn, and Mn are less than 2 before submergence (Table 2), suggesting that their contaminations are not a major concern according to the assessment criteria recommended by Han et al. [36] although moderate enrichment of these metals has been found in the upper reach (sites 1–3) [36]. In contrast, the average EF of As and Cd are greater than 2 before submergence (Table 2), suggesting that they are the major contamination. In fact, moderate to significant enrichment of As and Cd are found in the upper and low reaches (Table 2), which is consistent with the spatial patterns of heavy metals, suggesting that the main pollutions of As and Cd are correlated to anthropogenic activities [18]. The upper reach (sites 1–4) is near the industrial parks and urban, and the low reach (sites 9–12) is near large sewage outlet due to the development of agriculture [22,24].

After the inundation, EF (Hg), EF (Cd), and EF (Pb) increase and become the major concern contaminations with their average EF values greater than 2 (Table 2). The increase in EF (Cd), EF (Pb), and EF (Hg) are found in all the sampling sites, suggesting that

there are additional sources to the WLFZ in the submergence period [13]. During the submergence period, water transport in the WLFZ becomes more frequent, which might contaminate the reservoir by vehicle exhaust containing Hg [40].

#### 4.3. Source identification by factor analysis (FA)

FA allows identify the possible sources that influence soil quality [18]. A factor represents one type of possible pollution source. In this study, four factors are obtained, accounting for 86% of the total variance before submergence and 84% after submergence (Table 4), and the extracted factors contain critical information to explain metal contamination in the study region. Before submergence, Factor 1, accounting for 41% of the total variance, has the highest loadings of Cd, Pb, Cu, Zn, and Mn and medium loadings of As and Fe (Table 4), and can be considered as industrial wastewater source [28]. Frequent industrial activities result in the higher concentrations of Cd, Pb, Cu, Zn, and Mn in the upper reach (Fig. 2 and Table 2) [13], which reveals the contribution of industrial wastewater to these heavy metals pollution in the soil. Factor 2, accounting for 19% of the total variance with the highest loadings of Cr and Fe and intermediate loading of Zn (Table 4), could be considered as crustal source associated with Fe-oxides [35]. The results also show that the EF (Cr) is less than 1.5 (Table 2), which exhibits the contribution of natural rock weathering. Factor 3, which has the

**Table 4**  
Varimax rotated factor loading (PCA) and identified sources of heavy metals in soils of the water-level-fluctuation zone, the Three Gorges Reservoir, China.

(a) Before submergence					(b) After submergence				
Variable	Factor 1	Factor 2	Factor 3	Factor 4	Variable	Factor 1	Factor 2	Factor 3	Factor 4
Hg				0.97	Hg				0.98
As	0.52		0.68		As		0.76	0.35	
Cr		0.91			Cr		0.60	0.64	
Cd	0.83		0.30		Cd	0.60	0.55	0.33	
Pb	0.92				Pb	0.93			
Cu	0.87				Cu	0.88	0.34		
Zn	0.82	0.33			Zn	0.93			
Fe	0.41	0.79			Fe	0.33	0.77		
Mn	0.80				Mn	0.33	0.75		
SOC			0.90		SOC			0.88	
Eigenvalues	5.03	1.55	1.21	0.78	Eigenvalues	4.80	1.68	1.02	0.85
Percent of variance	41.22	18.58	14.77	11.11	Percent of variance	31.84	26.32	14.83	10.55
Cumulative percentage	41.22	59.80	74.56	85.68	Cumulative percentage	31.84	58.16	72.99	83.54
Possible source	Industrial wastewater	Crustal materials associated with Fe-oxides	Domestic sewage	Traffic exhaust	Possible source	Industrial wastewater	Crustal materials associated with Fe- and Mn-oxides	Crustal materials associated with organic matters	Ttraffic exhaust

Note: SOC: soil organic carbon.

**Table 5**Source contribution (%) and the estimated to observed ratios (*E/O*) of heavy metals using factor analysis–multiple linear regression (FA-MLR).

	Industrial wastewater	Crustal materials associated with Fe-oxides	Domestic sewage	Traffic exhaust	<i>E/O</i>	<i>R</i> <sup>2</sup>
(a) Before submergence						
Hg	11.0	4.7	4.1	80.0	1.00	0.97
As	34.3	16.6	45.2	3.9	1.00	0.80
Cr	15.8	72.7	10.4	1.2	1.00	0.88
Cd	59.0	6.6	21.3	13.1	1.03	0.82
Pb	73.3	20.0	0.6	6.1	1.00	0.91
Cu	62.2	14.8	5.3	17.7	1.01	0.87
Zn	50.3	20.4	17.2	12.1	1.00	0.90
	Industrial wastewater	Crustal materials associated with Fe- and Mn-oxides	Crustal materials associated with organic matters	Traffic exhaust	<i>E/O</i>	<i>R</i> <sup>2</sup>
(b) After submergence						
Hg	8.1	7.0	4.2	80.6	1.00	0.98
As	19.3	50.6	23.5	6.6	1.02	0.79
Cr	4.0	43.0	45.6	7.3	1.00	0.79
Cd	35.5	32.5	19.2	12.8	1.05	0.83
Pb	72.9	19.2	5.7	2.3	1.00	0.94
Cu	63.4	24.3	9.2	3.2	1.00	0.91
Zn	67.0	14.6	9.2	9.2	1.00	0.93

highest loadings of As and SOC and accounts for 15% of the total variance (Table 4), could be considered as domestic sewage source [28]. Previous study had interpreted that organic pollution could be attributed to the domestic sewage [28]. In the present study, we also find that places with density population and agriculture nearby often have higher concentration of As in the soil (*i.e.*, upper and low reach) (Fig. 2). Factor 4 has high loading of Hg (Table 4) and could be regarded as the traffic source [41]. Although the contamination of Hg is not a major concern before submergence, there is high enrichment in site 7 (*i.e.*,  $EF(Hg) > 2$ ) (Table 2) located near a big commercial harbor, *i.e.*, Wanzhou Harbor (Fig. 1). Therefore, the Hg pollution is attributed to the traffic exhaust.

After the inundation, Factor 1, with the highest loadings of Cd, Pb, Cu, and Zn and medium loadings of Fe and Mn, and accounting for 32% of the total variance (Table 4), could be considered as industrial source (Fig. 2 and Table 2) [28]. Factor 2, accounting for 26% of the total variance, has the highest loadings of As, Cr, Fe, and Mn and intermediate loadings of Cd and Cu (Table 4) and could be considered as crustal source associated with Fe- and Mn-oxides. The  $EF(As)$  and  $EF(Cr)$  are less than 1.5 (Table 2), suggesting that they might be entirely from crustal materials or natural weathering [35]. Factor 3, accounting for 15% of the total variance with the highest loadings of Cr and SOC and intermediate loadings of As and Cd (Table 3), could be considered as crustal source associated with organic matters [13]. The  $EF(Cr)$  is less than 1.5 (Table 2), suggesting that the contribution of crustal materials to the origination of Cr in a form which is associated with organic matters [13,35]. Factor 4, with high loading of Hg only (Table 4), could be contributable to the traffic source [41]. In the submergence season, the pollution of Hg is correlated to the non-point traffic exhausts in the TGR region [40].

#### 4.4. Source apportionment for heavy metals

After determining the possible sources by the FA, source apportionment of heavy metals was then computed using FA-MLR, a proven effective approach for quantifying contributions from varying sources [42,43]. Before submergence, As and Cd are the primary pollutants and the domestic sewage and industrial wastewater are the major pollution sources, which accounts over 45% for As and about 59% for Cd, respectively (Table 5). After submergence, the primary contaminations are Hg, Cd and Pb, and traffic exhausts and industrial effluents are the major contributors of these heavy metal pollutions (Table 5). Individually, traffic exhausts contribute

approximately 81% to Hg, and industrial effluents account about 36% for Cd and 73% for Pb (Table 5). The ratio between the estimated and observed values (*E/O*) of each element is around 1.00, suggesting acceptable results by the FA-MLR [37].

#### 4.5. Changes in heavy metals before and after submergence

Submergence could influence heavy metals in the riparian zone by fluvial transport and materials exchange between the uplands and riparian zone [5]. There are significant increase in the concentrations of Hg, Cd, Pb, Cu, and Zn, and decrease in As and Fe ( $p < 0.05$ ) (Tables 1 and 3) after inundation. During the submergence period, Hg, Cd, Pb, Cu, and Zn resulting from traffic exhaust and industrial wastes, might have been transported from the river system to the WLFZ by hydrodynamics [20,44]. The inundation would also deliver materials from the WLFZ to river by active materials exchange, resulting in the decrease in As and Fe (Table 3) [5]. Additionally, the contamination of As before submergence is mainly caused by domestic sewage runoff, and in winter (inundation season) the sewage runoff becomes smaller due to the dry season [28], leading to the decreased As (Table 3).

The heavy metal pollution in the WLFZ also changes by the submergence. Before the submergence, the major pollutants, As and Cd are mainly from domestic sewage and industrial wastewater discharged by the anthropogenic land-based point activities. After the inundation, the main contaminations are Hg, Cd, and Pb which are primary from traffic exhaust and industrial wastewater. The increased  $EF$  values of Hg, Cd, and Pb indicate the contribution of non-point pollutants to the WLFZ during the submergence period [5]. Moreover, another crustal source associated with organic matters are presented after the inundation (Table 3), and it is related with a layer of silty mud being deposited, *i.e.*, the increase in SOC and Cr, in the WLFZ during the submergence period (Fig. 2) [20].

Our results on the concentrations of Hg, Cd, Pb, Cu, and Zn are comparable with previous studies, while extremely high concentration of As occurs before the submergence in 2008 (Table 3). The higher levels of As might be attributed to the larger domestic sewage runoff, which is caused by the urbanization and economic development particularly in the recent years. However, after the inundation in 2009, increase in the inundated areas and introduction of the non-point sources by the submergence should have provided additional pollutants to the WLFZ, leading to the increases in Hg and Cd (Table 3).

## 5. Conclusion

Heavy metals show significantly spatial variability both before and after submergence in the soil of the water-level-fluctuation-zone (WLFZ) of the Three Gorges Reservoir, China. Elements including As, Cd, Pb, Cu, and Zn are higher in the upper and low reaches. The major pollutants are As and Cd before submergence, and Hg, Cd, and Pb after submergence by the EF assessment. The major pollutants (As and Cd) primarily originate from domestic sewage and industrial wastes before submergence, and the main contaminations (Hg, Cd, and Pb) after-submergence are primarily contributable to traffic exhaust and industrial effluents. Moreover, submergence results in deposition of Hg, Cd, Pb, Cu, and Zn by additional non-point source of pollutants and facilitate material exchange of As and Fe in the WLFZ. The results suggest that the shipping and the industrial waste waters should be regulated to protect the WLFZ in the Three Gorges Reservoir, China.

## Acknowledgements

This research is supported by the Executive Office of the State Council Three Gorges Construction Committee (SX2008-005; SX2010-014). We would like to thank Shuduan Tan, Zhixi Wang, Qiliang Yin and Chuan Wu for their assistance during fieldwork, and Pingcai Yan for the assistance on the laboratory analyses. Special thanks are also given to Professor Gianluca Li Puma and three anonymous reviewers for their constructive suggestions.

## References

- [1] C. González-Mačias, I. Schifter, D.B. Lluch-Cota, L. Mendez-Rodríguez, S. Hernandez-Vazquez, Distribution, enrichment and accumulation of heavy metals in coastal sediments of Salina Cruz Bay, Mexico, *Environ. Monit. Assess.* 118 (2006) 211–230.
- [2] S. Li, Z. Xu, X. Cheng, Q. Zhang, Dissolved trace elements and heavy metals in the Danjiangkou Reservoir, China, *Environ. Geol.* 55 (2008) 977–983.
- [3] S. Li, Q. Zhang, Risk assessment and seasonal variations of dissolved trace elements and heavy metals in the Upper Han River, China, *J. Hazard. Mater.* 181 (2010) 1051–1058.
- [4] S. Li, Q. Zhang, Spatial characterization of dissolved trace elements and heavy metals in the upper River (China) using multivariate statistical techniques, *J. Hazard. Mater.* 176 (2010) 579–588.
- [5] N.F.Y. Tam, Y.S. Wong, Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps, *Environ. Pollut.* 110 (2000) 195–205.
- [6] H. Feng, X. Han, W. Zhang, L. Yu, A preliminary study of heavy metal contamination in Yangtze River intertidal zone due to urbanization, *Mar. Pollut. Bull.* 49 (2004) 910–915.
- [7] L. Zhang, X. Ye, H. Feng, Y. Jing, T. Ouyang, X. Yu, R. Liang, W. Chen, Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China, *Mar. Pollut. Bull.* 54 (2007) 974–982.
- [8] K. Loska, D. Wiechula, Application of principal component analysis for the estimation of source of heavy metal pollution in surface sediments from the Rybnik Reservoir, *Chemosphere* 51 (2003) 723–733.
- [9] P. Censi, S.E. Spoto, F. Saino, M. Sprovieri, S. Mazzola, G. Nardone, S.I. Di Geronimo, R. Punturo, D. Ottonello, Heavy metals in coastal water systems: a case study from the northwestern Gulf of Thailand, *Chemosphere* 64 (2006) 1167–1176.
- [10] S. Qiao, Z. Yang, Y. Pan, Z. Guo, Metals in suspended sediments from the Changjiang (Yangtze River) and Huanghe (Yellow River) to the sea and their comparison, *Estuar. Coast. Shelf Sci.* 74 (2007) 539–548.
- [11] F.U. Amaya, L.M. Cristina, R. Enrique, L.F.M. Maria, Source identification of heavy metals in pastureland by multivariate analysis in NW Spain, *J. Hazard. Mater.* 165 (2009) 1008–1015.
- [12] A.J. Wang, J. Chen, Spatial variations in depth-distribution of trace metals in coastal wetland sediments from Quanzhou Bay, Fujian Province, China, *Chinese Geogr. Sci.* 19 (2009) 62–68.
- [13] W.G. Zhang, H. Feng, J.N. Chang, J.G. Qu, H.X. Xie, L.Z. Yu, Heavy metal contamination in surface sediments of Yangtze River intertidal zone: an assessment from different indexes, *Environ. Pollut.* 157 (2009) 1533–1543.
- [14] G.P. Glasby, P. Szefer, J. Geldon, J. Warzocha, Heavy-metal pollution of sediments from Szczecin Lagoon and the Gdansk Basin, Poland, *Sci. Total Environ.* 330 (2004) 249–269.
- [15] S. Caeiro, M.H. Costa, T.B. Ramos, F. Fernandes, N. Silveira, A. Coimbra, G. Medeiros, M. Painho, Assessing heavy metal contamination in Sado Estuary sediment: an index analysis approach, *Ecol. Indic.* 5 (2005) 151–169.
- [16] X.S. Wang, Y. Qin, Use of multivariate statistical analysis to determine the relationship between the magnetic properties of urban topsoil and its metal, S, and Br content, *Environ. Geol.* 51 (2006) 509–516.
- [17] F. Zhou, Y. Liu, H.C. Guo, Application of multivariate statistical methods to the water quality assessment of the watercourses in the Northwestern New Territories, Hong Kong, *Environ. Monit. Assess.* 132 (2006) 1–13.
- [18] B. Wu, D.Y. Zhao, Y. Zhang, X.X. Zhang, S.P. Cheng, Multivariate statistical study of organic pollutants in Nanjing reach of Yangtze River, *J. Hazard. Mater.* 169 (2009) 1093–1098.
- [19] Z.C. Zhong, D.H. Qi, The Illustrated Species Catalog and Biodiversity in the Hydro-fluctuation Belt of Three Gorges Reservoir, Southwest China Normal University Press, Chongqing, 2008.
- [20] E. Cebula, J. Ciba, Effects of flooding in southern Poland on heavy metal concentrations in soils, *Soil Use Manage.* 21 (2005) 348–351.
- [21] S.J. Xu, S.Q. Wei, D.T. Xie, Characteristics of heavy metals distribution in cultivated soil in Three Gorges Reservoir Area (TGRA), *J. Soil Water Conserv.* 17 (2003) 64–67.
- [22] L.L. Li, S. Zhang, J.H. Liu, X.L. Zhao, J.X. Gao, Investigation and evaluation on heavy metal pollution of water-level-fluctuating zone in Three Gorges Reservoir Area, *J. Soil Water Conserv.* 19 (2005) 127–130.
- [23] F. Yu, C. Zhang, S. Zhang, D.Y. Wang, Y.P. Huang, Contents and distribution of heavy metals in the draw-down zone of the Three-Gorges Reservoir Area, *J. Southwest Agric. Univ. (Nat. Sci.)* 28 (2006) 165–168.
- [24] J. Tang, S.J. Wang, S.H. Fu, Y.D. Sun, J.L. Lei, Soil environmental quality evaluation of the Three-Gorges Reservoir Region, *Acta Pedologica Sinica* 45 (2008) 601–607.
- [25] C.M. Zhao, W.L. Chen, H.D. Huang, Z.Q. Tian, Y. Chen, Z.Q. Xie, Spatial pattern of plant species diversity in the inundation and resettlement region of the Three Gorges Reservoir, *Biodivers. Sci.* 15 (2007) 510–522.
- [26] T. New, Z.Q. Xie, Impact of large dams on riparian vegetation: applying global experience to the case of China's Three Gorges Dam, *Biodivers. Conserv.* 17 (2008) 3149–3163.
- [27] Z.J. Lu, L.F. Li, M.X. Jiang, H.D. Huang, D.C. Bao, Can the soil seed bank contribute to revegetation of the drawdown zone in the Three Gorges Reservoir Region? *Plant Ecol.* 209 (2010) 153–165.
- [28] R.Z. Li, K. Shu, Y.Y. Luo, Y. Shi, Assessment of heavy metal pollution in estuarine surface sediments of Tangxi River in Chaohu lake basin, *Chinese Geogr. Sci.* 20 (2010) 9–17.
- [29] State Environmental Protection Administration of China (SEPA), Environmental Quality Standard for Soils (GB15618-1995), China Environmental Science Press, Beijing, 1995.
- [30] A.M. Idris, Combining multivariate analysis and geochemical approaches for assessing heavy metal level in sediments from Sudanese harbors along the Red Sea coast, *Microchem. J.* 90 (2008) 159–163.
- [31] Y.M. N'guessan, J.L. Probst, T. Bur, A. Probst, Trace elements in stream bed sediments from agricultural catchments (Gascogne region, S-W France): where do they come from? *Sci. Total Environ.* 407 (2009) 2939–2952.
- [32] P. Blaser, S. Zimmermann, J. Luster, W. Shotyk, Critical examination of trace element enrichments and depletions in soils: As, Cr, Cu, Ni, Pb, and Zn in Swiss forest soils, *Sci. Total Environ.* 249 (2000) 257–280.
- [33] J. Tang, Y.P. Zhong, L. Wang, Background value of soil heavy metal in the Three Gorges Reservoir District, *Chinese J. Eco-Agric.* 16 (2008) 848–852.
- [34] China National Environmental Monitoring Center (CNEMC), The Background Values of Chinese Soil, China Environmental Science Press, Beijing, 1990.
- [35] J. Zhang, C.L. Liu, Riverine composition and estuarine geochemistry of particulate metals in China-weathering features, anthropogenic impact and chemical fluxes, *Estuar. Coast. Shelf S.* 54 (2002) 1051–1070.
- [36] Y.M. Han, P.X. Du, J.J. Cao, E.S. Posmentier, Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China, *Sci. Total Environ.* 355 (2006) 176–186.
- [37] F. Zhou, H.C. Guo, L. Liu, Quantitative identification and source apportionment of anthropogenic heavy metals in marine sediment of Hong Kong, *Environ. Geol.* 53 (2007) 295–305.
- [38] R.A. Johnson, D.W. Wichern, Applied Multivariate Statistical Analysis, 5th ed., Prentice-Hall, NJ, 2002.
- [39] B. Helena, R. Pardo, M. Vega, E. Barrado, J.M. Fernandez, L. Fernandez, Temporal evolution of groundwater composition in an alluvial aquifer (pisuerga river, Spain) by principal component analysis, *Water Res.* 34 (2000) 807–816.
- [40] State Environmental Protection Administration of China (SEPA), Ecological and Environmental Monitoring Communique on the Three Gorges Project, China Environmental Science Press, Beijing, 2009.
- [41] J.H. Liu, Preliminary Study of Hg Pollution in the City of Beijing, Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 1997.
- [42] H. Pekey, D. Karaka, M. Bakoğlu, Source apportionment of trace metals in surface waters of a polluted stream using multivariate statistical analyses, *Mar. Pollut. Bull.* 49 (2004) 809–818.
- [43] Y. Song, S.D. Xie, Y.H. Zhang, L.M. Zeng, L.G. Salmon, M. Zheng, Source apportionment of PM<sub>2.5</sub> in Beijing using principal component analysis/absolute principal component scores and UNMIX, *Sci. Total Environ.* 372 (2006) 278–328.
- [44] C.X. Yun, Recent Evolution of the Yangtze Estuary, China Ocean Press, Beijing, 2004.
- [45] Z.X. Song, M. Gao, L.A. Wang, Z.F. Wang, D.T. Xie, J.C. Qin, Heavy metal concentrations in agriculture soil of the Three-Gorges Reservoir area and their pollution evaluation—taking Cu, Pb, and Zn as examples, *J. Agro-Environ. Sci.* 27 (2008) 2189–2194.